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Extrusion-based 3D printing of ceramic components

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Abstract

Engineering ceramics are becoming increasingly important in the nowadays-industrial landscape, thanks to the exceptional combination of good mechanical, thermal and chemical properties. Nevertheless, traditional ceramic manufacturing technologies lack the ability to compete in a market of customized complex components. Additive Manufacturing therefore provides an important contribution, given the nearly unlimited design freedom. This research aims at developing an extrusion-based AM technology using UV-curable dispersions. The homogeneity, rheology and printability of these dispersions, containing 22,5%vol to 55%vol ZrO_2 in different commercially available resins were investigated. A sintered density of 92% was obtained, proving the potential of the technology in development.

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Keywords: Additive manufacturing; Zirconia; UV-resin; Syringe extrusion; Productiontechnology

1. Introduction

Engineering ceramics, such as oxides, borides and carbides, receive increasing industrial interest. Due to their unique combination of mechanical, thermal and chemical properties, these materials find applications in different industries. The Freedonia Group expects the engineering ceramics market to reach 15.5 billion dollars in 2017 [1]. Especially Zirconium-dioxide (ZrO2, Zirconia) is an interesting material: due to its high toughness, thermal insulation, biocompatibility and ionic conductivity, it is nowadays used as material for e.g. body-implants, dental crowns, stamping dies, oxygen sensors and several micro components [2].

The manufacturing of ceramic components consists nowadays of a series of discrete production-steps, as can be seen in Fig. 1. Among them, green- and final machining (e.g. grinding and polishing) are the most cost-, labor- and tool-intensive. Moreover, conventional shaping techniques such as Ceramic Injection Molding (CIM) and Gel Casting, which involve the use of a tailored mold, are only economically competitive for large-size batches and the production of simple and medium-complex ceramic components. Furthermore, the production of highly complex 3D shapes, micro features, or structures with tailored porosity, such as scaffolds, is still seen as a major limit [2–4].

Additive manufacturing (AM) offers new opportunities in the gamma of shaping techniques for ceramics. Thanks to its (almost) unlimited freedom in design and flexibility, AM enables the production of customized and 3D complex shaped forms, even in small-size batches and with a limited time-to-market [5].

The feasibility of different AM processes, such as Stereolithography (SLA) [6], Lithography-based Ceramic Manufacturing (LCM) [7], Freeze-Form Extrusion (FFE) [8], Selective Laser Sintering (SLS) [9], Fused Deposition of Ceramics (FDC) [10] and Robocasting [11] has recently have been investigated for the production of ceramic components.

Most of these techniques make use of a composite ceramic-binder material, of which the binder is solidified, for the shaping of the green product. This latter is subsequently subjected to firing, to remove the binder and sintering in order to achieve a dens ceramic component.

SLA adopts UV-curable resin as a binder, mixed with ceramic powder. The resin is selectively cured by means of an UV-laser, providing the necessary consistence to the green product, and is subsequently removed by firing.

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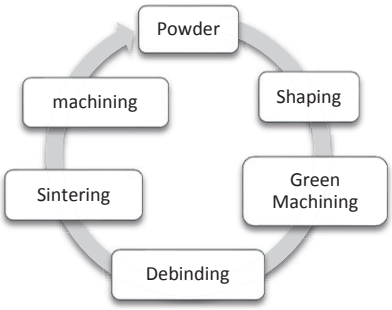


Fig. 1 – Conventional production cycle

After sintering of this fired product, a density of nearly 98% is achievable [6,12]. However, a full vat of particle-filled UV-resin is needed, which is both cost- and material-inefficient.

Indirect SLS uses alumina-polypropylene (PP) composite particles. The PP-phase functions as binder and it is selectively solidified by means of a laser. Recent research indicates that a density of up to 93% after Warm Isostatic Pressing is achievable [9]. However, further research is needed to augment this density after sintering. Besides, coating the particles with the PP-phase induces an extra step.

FDC employs a thermoplastic filament, filled in with ceramic particles. This filament is heated up to made the binder viscous, and subsequently extruded through a nozzle. Upon deposition, the binder cools and solidifies, trapping the ceramic particles and giving the green product a high strength. Using this technique, sintered densities up to 97% have been achieved [10]. However, a filled in thermoplastic filaments, made within close tolerances is needed.

Finally, Robocasting extrudes aqueous low-organic binder dispersion, containing up to 60 %vol of ceramic particles. Because of the high content of ceramic particles, the dispersion becomes dilatant upon minimal evaporation of the binder. Research indicates the possibility of producing parts with a final density of more than 95% [11]. However, a rigorous control of the drying conditions and rheological behavior of the dispersion is required to achieve adequate dimensional stability. Another important disadvantage is distinct stair casing, due to the low strength of the green product [13].

The present research specifically aims at developing a novel Additive Manufacturing process that combines the strengths of the aforementioned techniques through the combination of the economic usage of material of the extrusion process, as used in Robocasting and FDC, with the high green strength of UV-curing techniques such as LCM and SLA. This is achieved through the preparation of a dispersion, based on ceramic powders and UV-resin. This dispersion is subsequently deposited using a syringe-based 3D printing equipment, while being cured using a power-LED source.

2. Experimental set-up

This section provides a description of materials, methods and tools adopted for the preparation and characterization of the dispersions. The 3D printing method is also described.

2.1. Materials

Commercial yttrium-stabilized Zirconia (TZ-3YE, Tosoh Corp, Tokyo) nanoparticles (D_{50} = 0.6 μm) of high purity (>99,9%) were chosen as ceramic compound for the sake of lowering the sintering temperature. A measure of the maximal particle size (D_{max} = 4 μm) is needed in order to determine the homogeneity of the dispersion. Two commercially available UV (Ultra-Violet) curable resins were used as binder: XC11122 (DSM) and UV-A 2137 (Sadechaf),. The properties of the resins are listed in Table 1.

Table 1 – Properties of the UV-resins

Property	XC 11122	UV-A 2137
Viscosity (20°C)	260 mPa.s	750 mPa.s
Density	1.13 g/cm^3	1.05 g/cm^3
$E_{treshold}$	11.15 mJ/cm^2	1000 mJ/cm^2
T_{max}	46ºC	30ºC
Spectrum	±355 nm	320–355nm

2.2. Preparation of the dispersion

In order to achieve a homogenous dispersion, the zirconia particles were dispersed into the UV-resins for 24 hours using the “solution-mixing” (SM) principle, by means of a Turbula T2-F shaker-mixer. The mixture was then placed in an opaque container, along with zirconia mixing balls (diameter = 10mm) and 15 ml of ethanol; this latter to decrease the viscosity, so that formed agglomerates can be broken by the mixing balls. The ethanol was subsequently evaporated in a darkroom, at 45ºC for 48 hours. The low temperature was specifically chosen to avoid thermal polymerization, which renders the dispersion waste. Samples were also prepared using mechanical mixing (M) of the dispersion in order to determine whether a less time-consuming method of homogenization could be feasible.

Dispersions of different compositions (Φ), containing 22.5; 25; 27.5; 30; 45 and 55 %vol zirconia particles mixed in the two UV-resins, were prepared using both mixing techniques.

2.3. Characterization of the dispersion

The quality of the prepared dispersions was investigated considering the homogenization, rheological behavior and printability. At first, a clear distinction between a 'depositable' and a 'printable' dispersion has to be made. For sake of clearness, a prepared dispersion is considered 'depositable' when the used Additive Manufacturing machine is able to extrude it (i.e. the viscosity remains below a certain threshold). 'Printable' dispersions instead are homogenous preparations, which possess a given viscosity so that tracks of material remain their shape during processing, but also slump a certain amount to assure connection between the tracks (desirable rheological behavior). This aspect is crucial to reach sufficient density of the material after sintering, while maintaining adequate dimensional control. Tools and methods used for characterization are described here below more in detail.

Homogeneity of the dispersions. Since agglomerates have a catastrophic influence on the rheology of the dispersion and the quality of the sintered product, the achievement of a homogenous dispersion is crucial. This was tested by inspecting fully polymerized samples of the different compositions, as described in 2.2, on a Philips XL30 FEG SEM. Agglomerates, formed during the mixing process, can be distinguished from the individual Zirconia particles by bringing the particle distribution of the delivered powder into account (larger particles than D_{max} of the starting powder are supposed to have formed during the preparation). Locally high concentrations of zirconia are visualized by Back Scatter Electrons (BSE) technique, where white spots in the image denote locally high concentrations of heavy elements, in this case the zirconia. To ensure that no UV-resin was lost during evaporation of the ethanol, the composition of the different dispersions was also tested using Energy Dispersive X-Ray Spectroscopy (EDX).

Rheology of the dispersions. The rheology of the dispersions was tested using an Anton Paar Physica MCR501 rheometer with cone-plate geometry (CP25-2), and a shear rate varying from $100s^{-1}$ to $0.1s^{-1}$. No rheology tests were conducted on the 45%vol and 55%vol dispersions, prepared with both techniques because they were ascertained to be not depositable.

Printability of the dispersion. In order to achieve good dimensional accuracy and a high density after sintering, the slumping of a deposited track needs to be controlled during the polymerization of the dispersion. To evaluate this aspect, the cross-sectional shape and dimensions of a single deposited track was acquired by means of a GOM ATOS Compact Scan 2M (measuring volume 30 x 35 mm and accuracy 10 μm) before and after polymerization. Scans were specifically taken at 1 minute after the deposition, and after the polymerization. Cylinders were fitted through the thus acquired point-cloud, and the respective diameters are therefrom extracted. Shape stability is then evaluated based on the change in diameter after one minute and after curing as compared to the diameter of the deposited track (in this case 0.75 mm).

Deposition was made with a syringe-based 3D printer (see section 2.4), which is programmed to print tracks of 30mm in length and 0.75mm in diameter. Polymerization was subsequently achieved with a 400nm UV-led source (Clearstone CF2000), capable of delivering up to $4W/cm^2$. The power of the source and the illumination time are both adjustable. The composition (Φ) of the dispersion, method of preparation, power intensity and time of exposure for polymerization were all considered for investigation and their possible influence on printability studied by means of two full factorial designs. Table 2 lists the levels for each input factor.

Table 2 – Factorial table

Factor	Code	(-)	(+)	Replicas
Time (s)	A	30	120	4
Intensity (W/cm^2)	B	0.8	4	4
Φ (%vol)	C	27.5	30	4
Method	D	SM	M	4

2.4. Printing of ceramic samples

Ceramic beam were printed using a syringe based printing equipment (Fab@Home V1), equipped with a 0.5mm nozzle. Fig. 2 shows such a sample. A dedicated controller was installed to enable control of the machine with specific machine code. During the printing, the component was irradiated with 400nm UV-light with an energy density of $4W/cm^2$.

Removing the UV-resin was obtained by firing the samples at 0.1ºC/min until a temperature of 600°C was reached. This temperature was maintained for 2 hours. The needed temperature for firing was achieved by using a SDT QA600 (TA instruments) DSC/TGA analyzer.

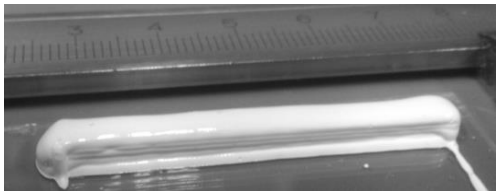


Fig. 2 – Printed sample using the 30%vol Zirconia dispersion

Afterwards, the samples were sintered at a temperature of 1450 ºC for two hours. During the process, samples were placed in an alumina powder bed, which is coarse enough to prevent sintering to the sample, in order to ensure dimensional stability. The density of the material

after sintering was measured using the Archimedes method.

3. Results and discussion

3.1. Homogeneity of the dispersion

As can be seen in Fig. 3(a), homogeneity can be achieved for a dispersion containing up to 55%vol concentration of zirconia, dispersed into XC11122 UV resin, using the solution mixing technique (SM). On the contrary, no satisfying results could be achieved with the same technique and UV-Acryl 2137 resin. BSE pictures (Fig. 3(b)) reveale locally high concentrations of zirconia, indicating a lack of homogenization. This could be explained by the lack of repulsive forces between the particles to oppose the attracting Vander Waals forces [14]. Therefore, UV-A 2137 resins are unsuitable for the preparation of ceramic dispersion for extrusion-based 3D printing of ceramics. Similar conclusions can be made for the mechanical mixing technique. As shown in Fig. 3(c), agglomeration of zirconia is severe in the mechanically mixed dispersion of 30%vol Zirconia in XC11122.

No significant amount of resin was lost during the evaporation of the ethanol, as was confirmed by the EDX analysis.

3.2. Rheology of the dispersion

Fig. 4 shows the results of the rheological measurements, made for the different dispersions. As shown, all the samples exhibit a shear thinning behavior, which promotes the deposition process. It can also be noted that the viscosity increases along with the amount of ceramic particles. This is in agreement with the Krieger-Dougherty theory. Viscosity at 'zero-shear' is approximated by the viscosity, measured at $0.1s^{-1}$.

The experimental points were fitted using the Cross model (1).

$$\mu_{eff}(\dot{\gamma}) = \frac{\mu_0}{1+\left(\frac{\mu_0\dot{\gamma}}{\tau^*}\right)^{1-n}} \quad (1)$$

Where μ_{eff} is the viscosity, μ_0 is the zero shear viscosity and τ and n are fitting constants. The shear-rate during extrusion in the nozzle is calculated via equation (2).

$$\dot{\gamma} = \frac{8Q}{3\pi a} \quad (2)$$

Herein is "Q" the volumetric flow-rate (mm^3/s) of the material, "a" the nozzle radius (mm) and "γ" the shear rate (s^{-1}) during extrusion. Keeping in mind that the movement speed of the nozzle is 5mm/s and the nozzle-diameter and layer thickness are 0.75mm, the shear rate in the nozzle during printing could be calculated to be approximately $26s^{-1}$. This value is indicated in Fig.4 as a vertical line. The viscosity in the nozzle for the 22.5; 25; 27.5 and 30%vol dispersion could be then calculated (1) as 1.19; 4.8; 5.9 and 28.6 Pa.s, respectively. Based on the testing of the printability of the dispersion, a desirable rheology can be defined later on.

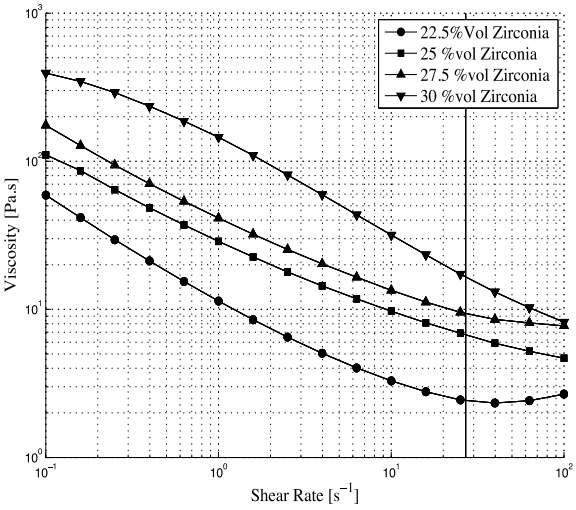


Fig. 4 – Viscosity as function of the shear rate for the different tested dispersions (6). The vertical line depicts the shear rate, occurring in the nozzle during the print process.

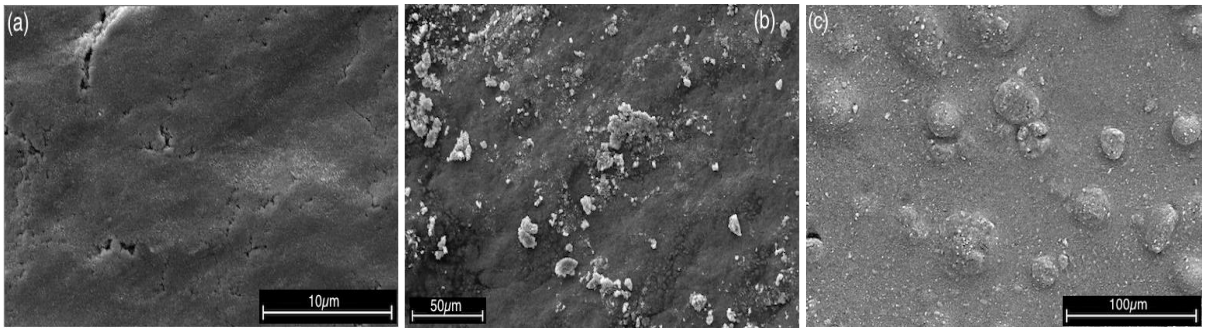
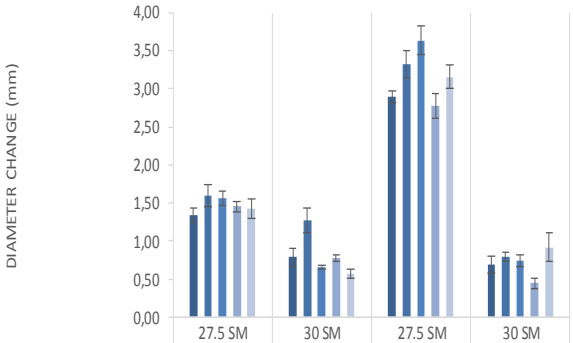


Fig. 3 – BSE pictures of different tested dispersions. (a) SM 55%vol Zirconia in XC11122. (b) SM 55%vol Zirconia in UV-A 2137. (c) M 30%vol Zirconia in XC11122.

3.3. Printability

Fig. 5 plots the change in diameter of the deposited tracks after one minute and after polymerization, as a function of the composition, mixing method and settings of the light source (time and intensity). The method, stated in sect. 2.3, is used for the estimation of the shape stability, and thus the desired rheological behavior of the dispersion. Table 3 also lists the results of the ANOVA analysis. The higher order interactions are neglected in because their impact was found to be negligible.

As shown, shape stability upon deposition (uncured tracks after one minute) is largely influenced by the amount of ceramic particles in the dispersion (ϕ, factor C): a higher amount of ceramic particles leads to a more stable shape, because of the higher 'zero-shear' viscosity of such dispersion. In addition, the mixing method (factor D) and the interaction between the composition and mixing method have a significant influence. This latter can be explained by the formed agglomerates in the mechanically mixed dispersions. These agglomerates influence the rheological behavior of the dispersion, and therefore the shape stability of the track. The ANOVA analysis with a confidence level of at least 98%, shown in Table 3, proves these statements.



	27.5 SM	30 SM	27.5 SM	30 SM
Uncured after 1 minute	1,34	0,79	2,89	0,69
30s @ 0,8 W/cm2	1,60	1,28	3,33	0,80
120s @ 0.8 W/cm2	1,56	0,66	3,64	0,75
30s @ 4W/cm2	1,46	0,78	2,78	0,45
120s @ 4W/cm2	1,42	0,57	3,16	0,92

Fig. 5 – Positive change in diameter of a track under different conditions. The number on the x-scale depicts the %vol of ceramic particles, the letter the method of homogenisation.

During curing, the irradiation time (factor A), composition (factor C) and preparation method (factor D) are found to be the most significant parameters (Table 3, after curing). It should however be observed that the R^2 value of this ANOVA is too low to make any valid conclusions. This can be accredited to the lack of significance of the irradiation, which is in contradiction with relevant literature on UV-based dispersions.

Based on the achieved result, the most homogenous, printable dispersion is found to be the solution mixed 30%vol Zirconia in XC11122 UV resin.

3.4. Production of ceramic components

Zirconia samples were produced with the 30%vol XC11122 UV-based dispersion using the modified Fab@Home 3D-printer, based on a layer-by-layer strategy. By using iteratively defined parameters, beams with a geometric accuracy within the tolerances of the machine could be produced. The used UV irradiation (4W/cm^2, 400nm) however was found to be insufficient to polymerize a complete layer of the component. As a result, the lower layers were more sensitive to slumping. Moreover, incomplete curing of internal structures caused problems during the firing of the UV-resin. As solution, an extra thermal curing step was added; the printed samples were placed in oven for 96 hours at a temperature of 60ºC before de-binding the material. This can be avoided through complete polymerization of the dispersion. Achieving this through the usage of an improves setup is planned for future research.

Sintering of the products was also applied as described in sect. 2.4. Due to extensive shrinking, the components break apart in smaller pieces. Increasing the amount of ceramic particles in the dispersion might solve the problem. But to maintain the rheological properties, repulsive forces should be induced, e.g. by adding steric dispersants. The density of the pieces was finally measured using the Archimedes principle. A density of 92% was achieved, showing the potential of the method in development.

Table 3 – ANOVA analysis of the shape stability of the uncured and cured tracks. Only first order factors and significant interactions are shown. Four replicates four each experiment were made.

	Uncured				After curing			
	DF	SS	MS	P	DF	SS	MS	P
A					1	0.09	0.09	0.02
B					1	0.03	0.03	0.2
C	1	29.7	29.7	0	1	0.68	0.68	0
D	1	8.7	8.7	0	1	0.14	0.14	0.01
CD	1	11.4	11.4	0				
ε	59	5.5	5.5		48	0.86	0.02	
Σ	63	56.2			63	2.1		
	R^2 = 91%				R^2 = 59%			

4. Conclusion

Due to the unique combination of mechanical, thermal and biological properties, engineering ceramics are gaining an increasing attention in the industrial

environment. Economical production of small-scale, customized, complex ceramic components however, technical issues and high costs remain an important drawback. Additive Manufacturing of engineering ceramics can therefore be an important addition to the nowadays-existing gamma of production techniques for ceramic processing, especially in the segment of mass-customization. In order to combine the high shape stability and green strength of UV-curing techniques (SLA, LCM) with the economical usage of base material of extrusion based techniques, a novel syringe based AM process, based on a UV-dispersion, has been developed and tested.

At first, dispersions containing Zirconia particles, mixed in commercially available UV resins, were prepared and analyzed with respect to homogeneity, rheology and printability. Different compositions, mixing methods and curing parameters were investigated. Based on the achieved results, 30%vol zirconia dispersions in commercial XC11122 UV-resin, prepared using the "solution mixing" principle, showed the most desirable properties such as a suitable homogeneity and shape stability. Viscosity in the nozzle and on the platform (zero-shear) was measured to be 28.6Pa.s and 400Pa.s, respectively.

Printing tests were also conducted. Production of simple ceramic beams pointed out arguments for future improvements. At first, the used UV-source revealed to be inadequate for the intended process, due to a too low irrandiance and a non-optimal match with the polymerization wavelength of the used resin. This resulted into partial polymerization of the printed layers, and the need for an extra, thermal polymerization-step. A better-matched UV-source with a higher irradiance is thus desirable, in order to eliminate this extra, time consuming step.

Firing and sintering of the components also proved to be challenging. Specifically, a large shrinkage was experienced during sintering, leading to distinct part cracking. This is most likely caused by an insufficient amount of ceramic particles in the dispersion. Future research will therefore focus on augmenting the amount of ceramic particles, while keeping the rheological behavior unchanged. This can e.g. be achieved through the introduction of steric repulsive forces in the dispersion. In this context, also other resins can be used.

On the other hand, a density of about 92% could be achieved after sintering, thus proving the potential of the technique under development.

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